



Sustainable functionalization of sp^2 carbon allotropes

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Objectives of the research activity

- ➡ To functionalize sp^2 carbon allotropes with sustainable, facile, versatile methods, preserving the sp^2 hybridization
- ➡ To reduce the synthetic footprint in carbon allotropes functionalization



☞ To take advantage of the **nanosize of the carbon substrate**



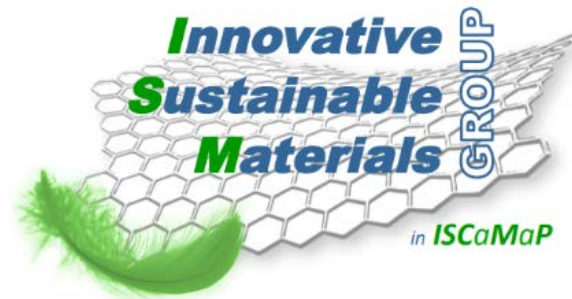
☞ to understand

the **mechanism of functionalization**

the **structure of functional carbon allotropes**

Functionalized carbon allotrope as platform chemical?

Functionalizing agents for sp^2 carbon allotropes.
From
biosourced molecules
and large scale industrial products

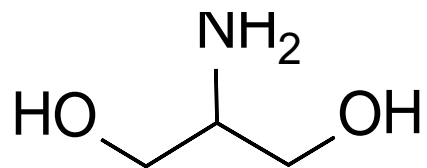
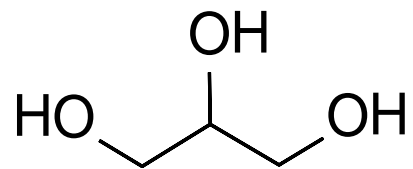


Functionalizing agents for sp^2 carbon allotropes from biosourced molecules

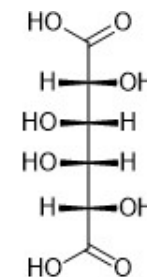
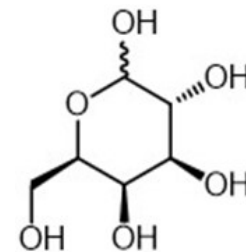


Biosourced molecules. A couple of examples

Glycerol, Sugars

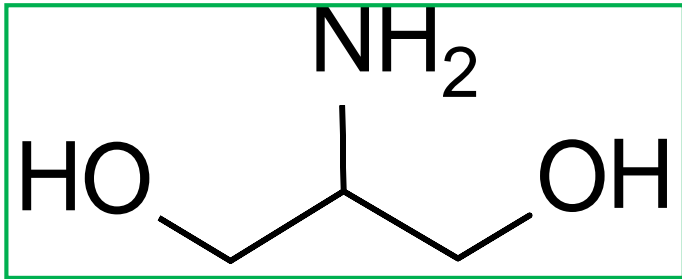
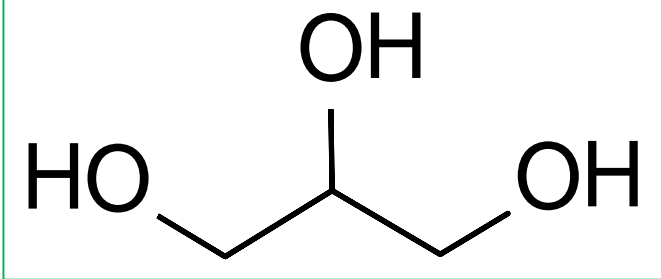


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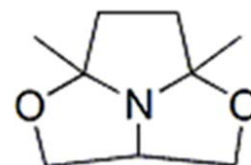
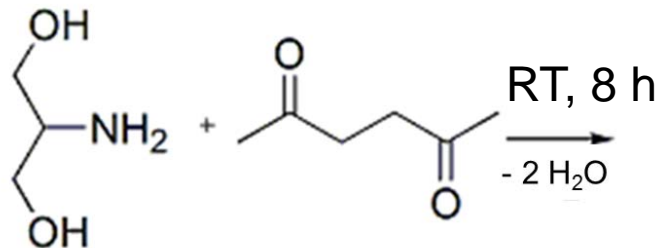
...

From glycerol to serinol

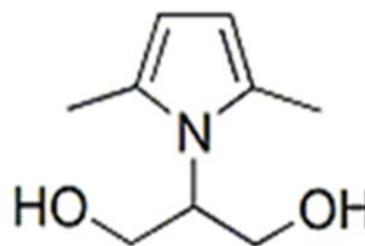


Reaction of serinol with a dicarbonyl compound

Sustainable
synthesis



Δ 180°C, 3 h



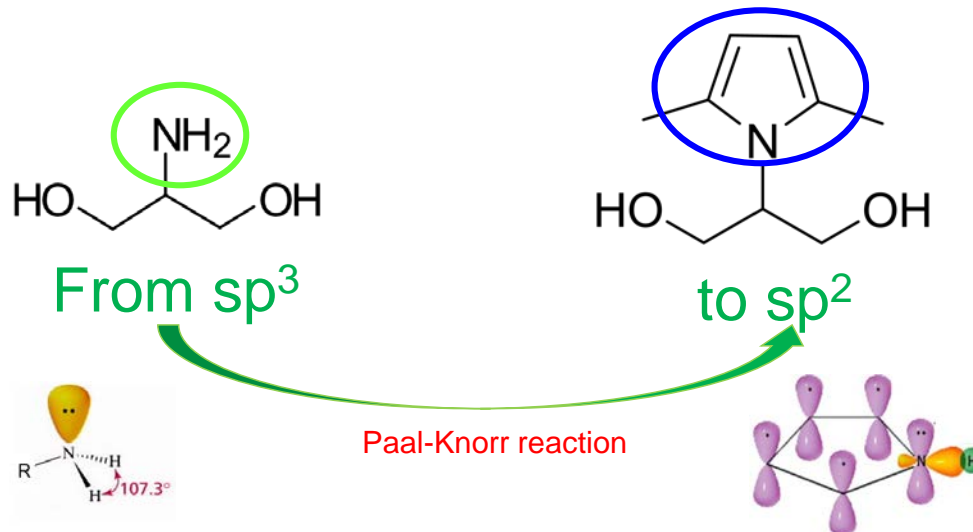
Serinol pyrrole - SP

No solvent
By product H_2O

2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol

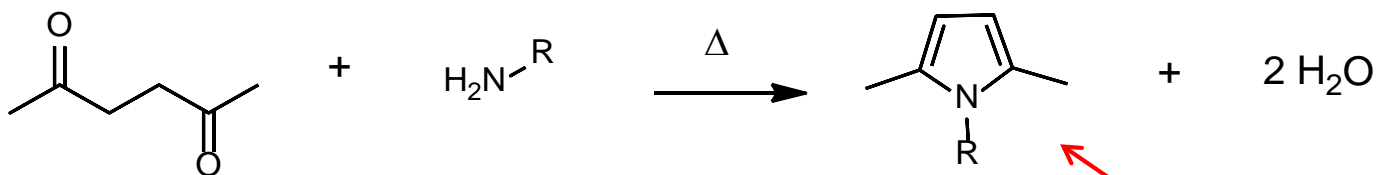
- V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio *WO 2015 189411 A1*
- M. Galimberti, V. Barbera, A. Citterio, R. Sebastiano, A. Truscillo, A. M. Valerio, L. Conzatti, R. Mendichi, *Polymer*, vol 63, 20 April 2015, Pages 62–70
- M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini, *RSC Adv.*, 2015, 5, 81142-81152 DOI: 10.1039/C5RA11387C
- V. Barbera, S. Musto, A. Citterio, L. Conzatti, M. Galimberti, *eXPRESS Polymer Letters* 2016, 10 (7) 548–558

Neat synthesis of Serinol pyrrole



- ➡ Yield: at least 96%
- ➡ Atom efficiency: 85%
- ➡ Easy procedure
- ➡ No solvent
- ➡ By product: H₂O

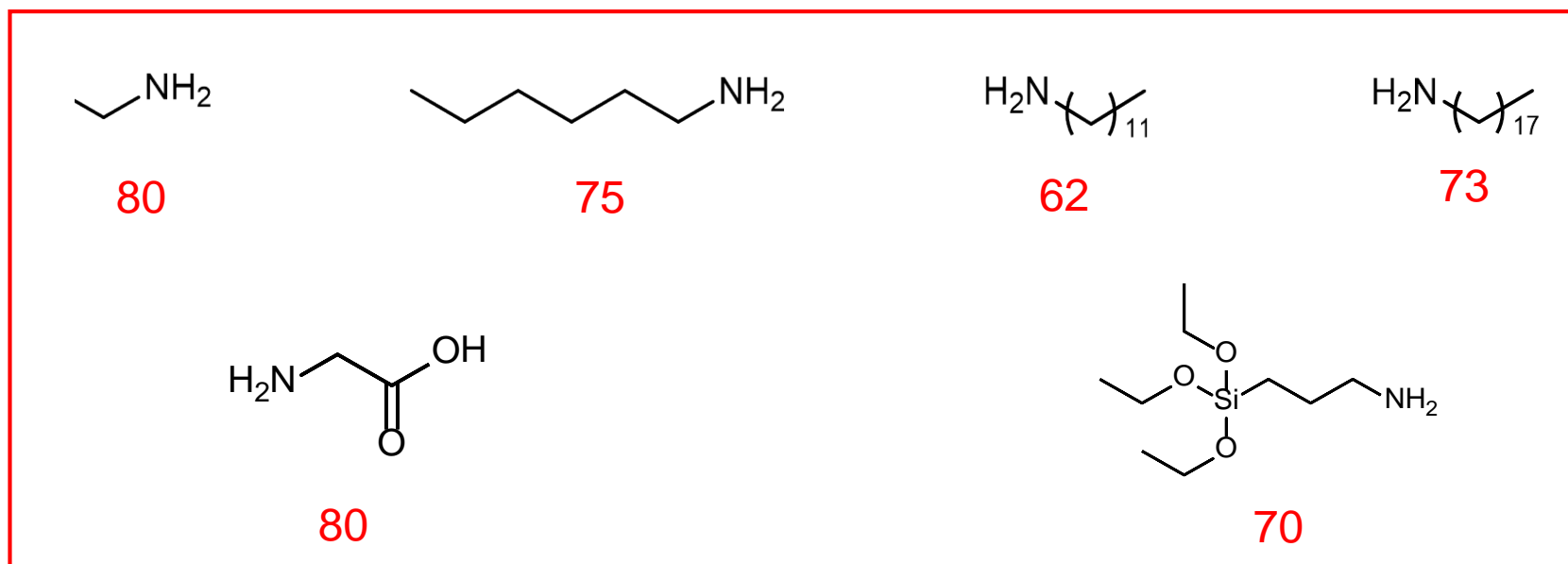
Pyrrole compounds (PyC) from neat Paal Knorr reaction



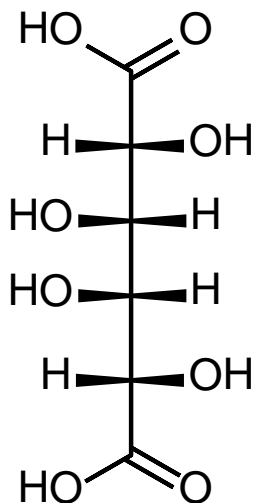
Same reaction conditions used for SP

PyC

Yield %



Chemicals from sugars. Galactaric Acid



IUPAC: (2R,3S,4R,5S)-2,3,4,5-tetrahydroxyhexanedioic acid

Common nomenclature: **mucic acid**

Formula: $C_6H_{10}O_8$

210.14 Da

- ➡ Symmetrical structure: achiral
- ➡ Platform molecule
- ➡ Not toxic, Biocompatible

Production: 38,000 tonn/year

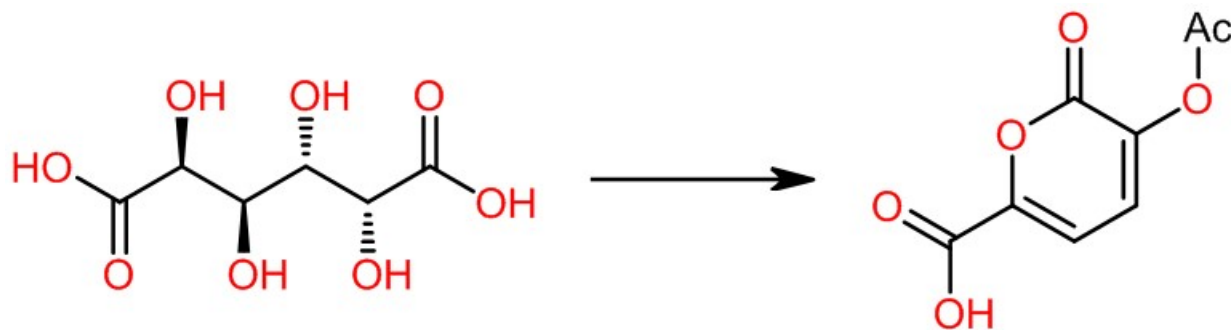
Cost: 4-10 \$/kg

R&D to improve production techniques



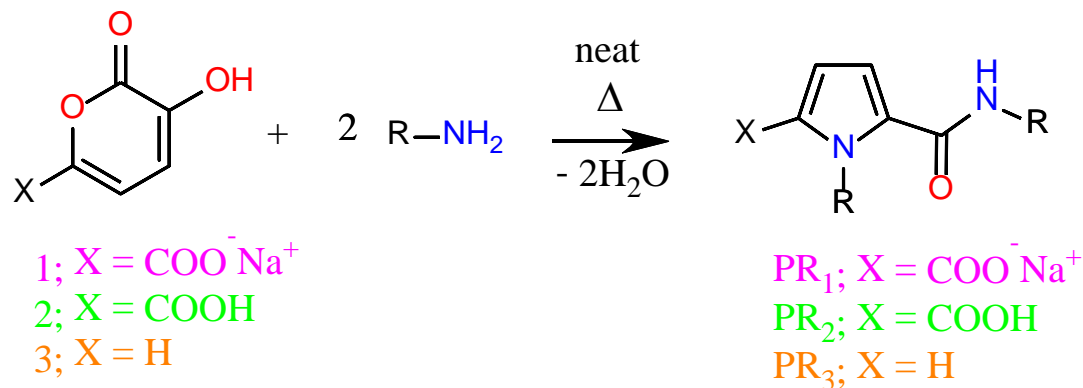
unlock its potential as a platform chemical

Synthesis of Pyrone Derivatives from Galactaric Acid



- ➡ Easy procedure
- ➡ High Conversion
- ➡ High Atom efficiency

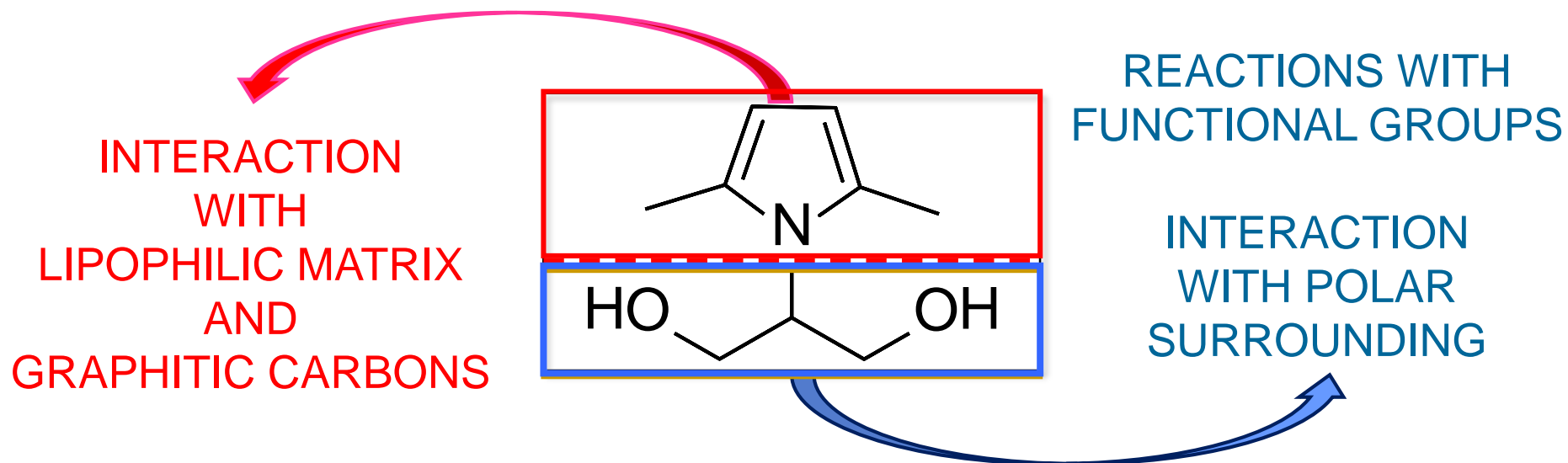
Synthesis of Pyrrole Derivatives from 2-Hydroxypyrones



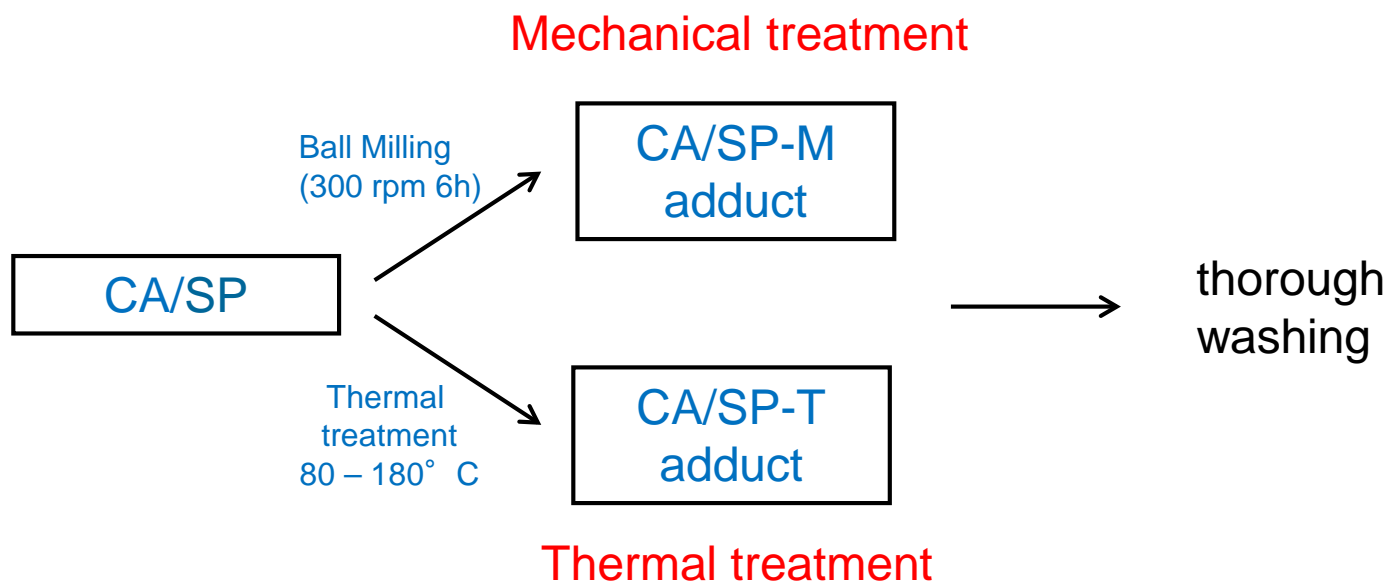
Subs.	Amine (equiv.)	T (° C)	t (h)	Conv. %	PR1 (Yield %)	PR2 (Yield %)	PR3 (Yield %)
1	Ethanolamine (5)	50	24	45	35	-	6
1	Ethanolamine (10)	50	63	98	94	-	0.6
1	Octylamine (10)	50	43	79	76	-	3
2	Ethanolamine (6.0)	50	24	100	-	95	0.6
2	Isoserinol (5.9)	50	26	98	-	95	0
2	Serinol (5.9)	70	21	97	-	93	6
2	Benzylamine (5.4)	75	20	92	-	71	21
2	Octylamine (10)	65	23	100	-	87	7
3	Ethanolamine (6)	50	24	100	-	-	75
3	Octylamine (10)	65	24	100	-	-	80

Functionalization of sp^2 carbon allotropes with the "pyrrole chemistry"

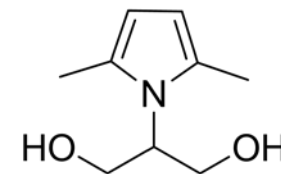
Serinolpyrrole: *Janus* molecule



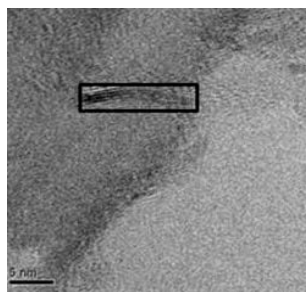
Adducts of SP with CA - Preparation



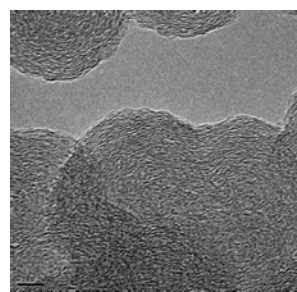
High yield of functionalization!



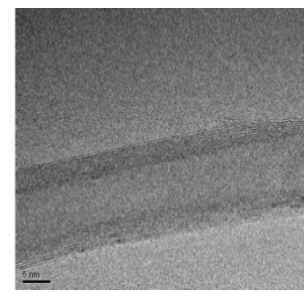
High surface area graphite



Carbon Black



Carbon Nanotubes



BET Surface area:
[m²/g]

300

77

275

Yield (%)*:

96

82

92

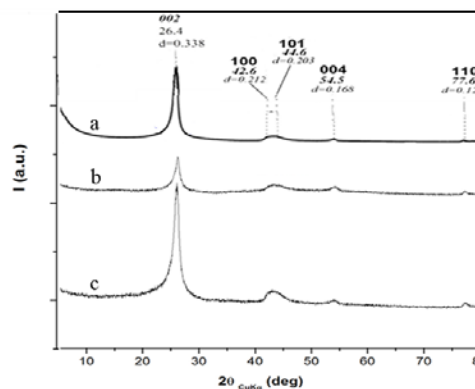
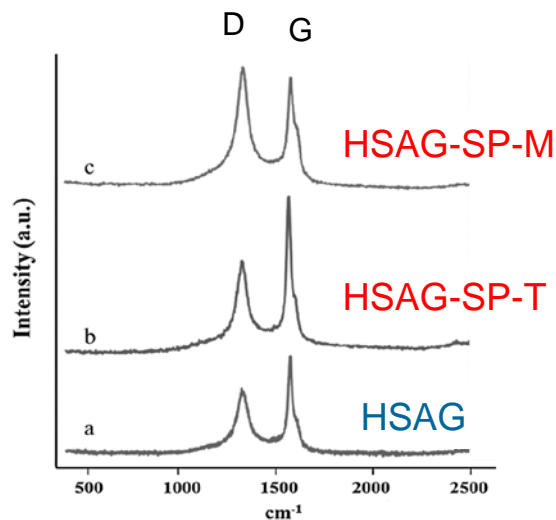
*estimated through:

$$\text{Functionalization Yield (\%)} = 100 * \frac{\text{SP mass \% in (CA-SP adduct) after acetone washing}}{\text{SP mass \% in (CA-SP adduct) before acetone washing}}$$

Adducts of SP with HSAG

- Functional groups up to 20%
- In plane order substantially unaltered
- No expansion of interlayer distance

Preserved sp^2 hybridization

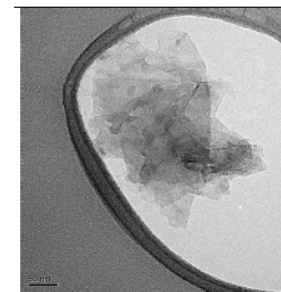


HSAG

HSAG-SP-M

HSAG-SP-T

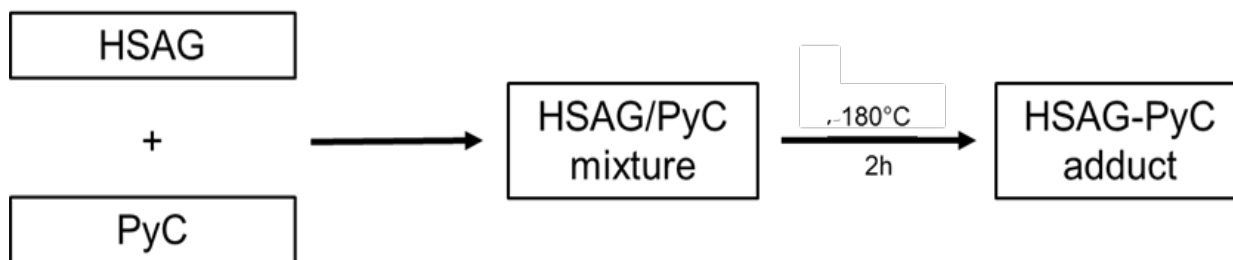
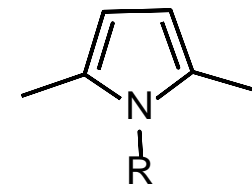
Few layers graphene



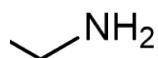
From water suspension

Results from elemental, TGA, IR, XPS, Raman, XRD, HRTEM analysis

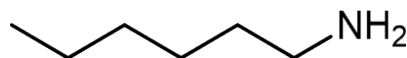
HSAG / PyC adducts



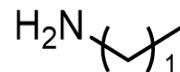
Functionalization Yield %



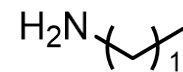
73



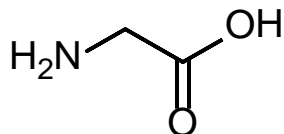
87



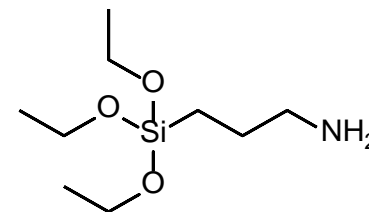
80



98



82



78

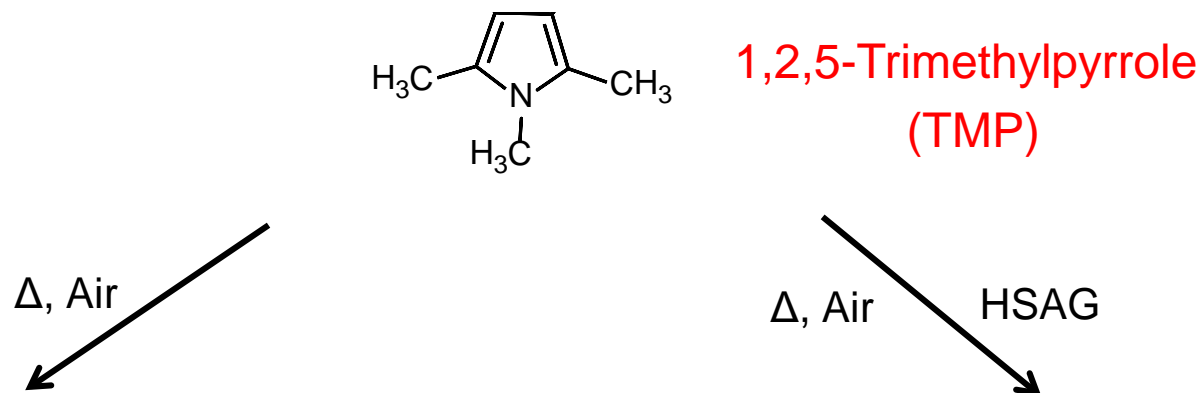
Why such a high yield of functionalization?



Mechanism of the functionalization reaction

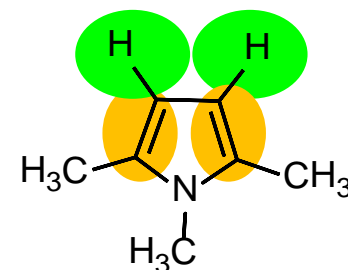
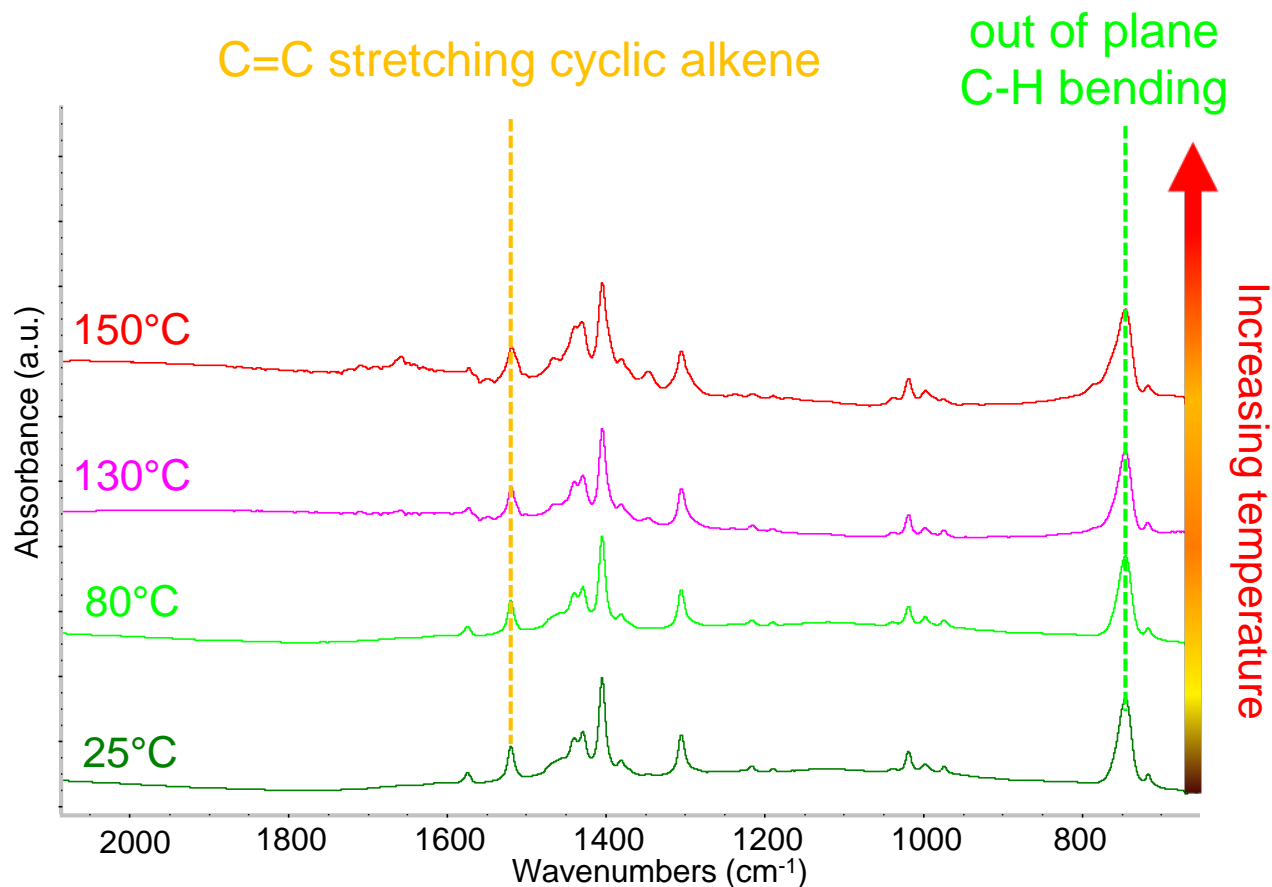
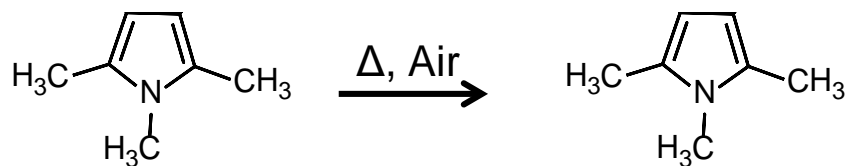
Mechanism of the functionalization reaction

Investigation with a model compound

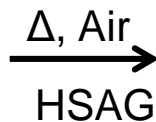
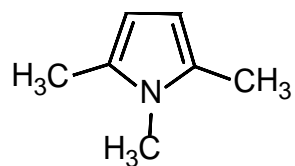


- ☞ Analysis of: liquids, HSAG/TMP adducts
- ☞ FT-IR and $^1\text{H-NMR}$ spectroscopies
- ☞ FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling

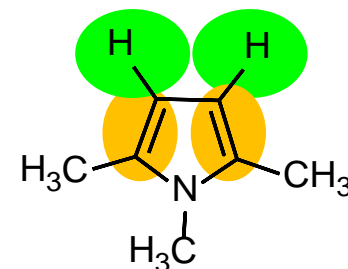
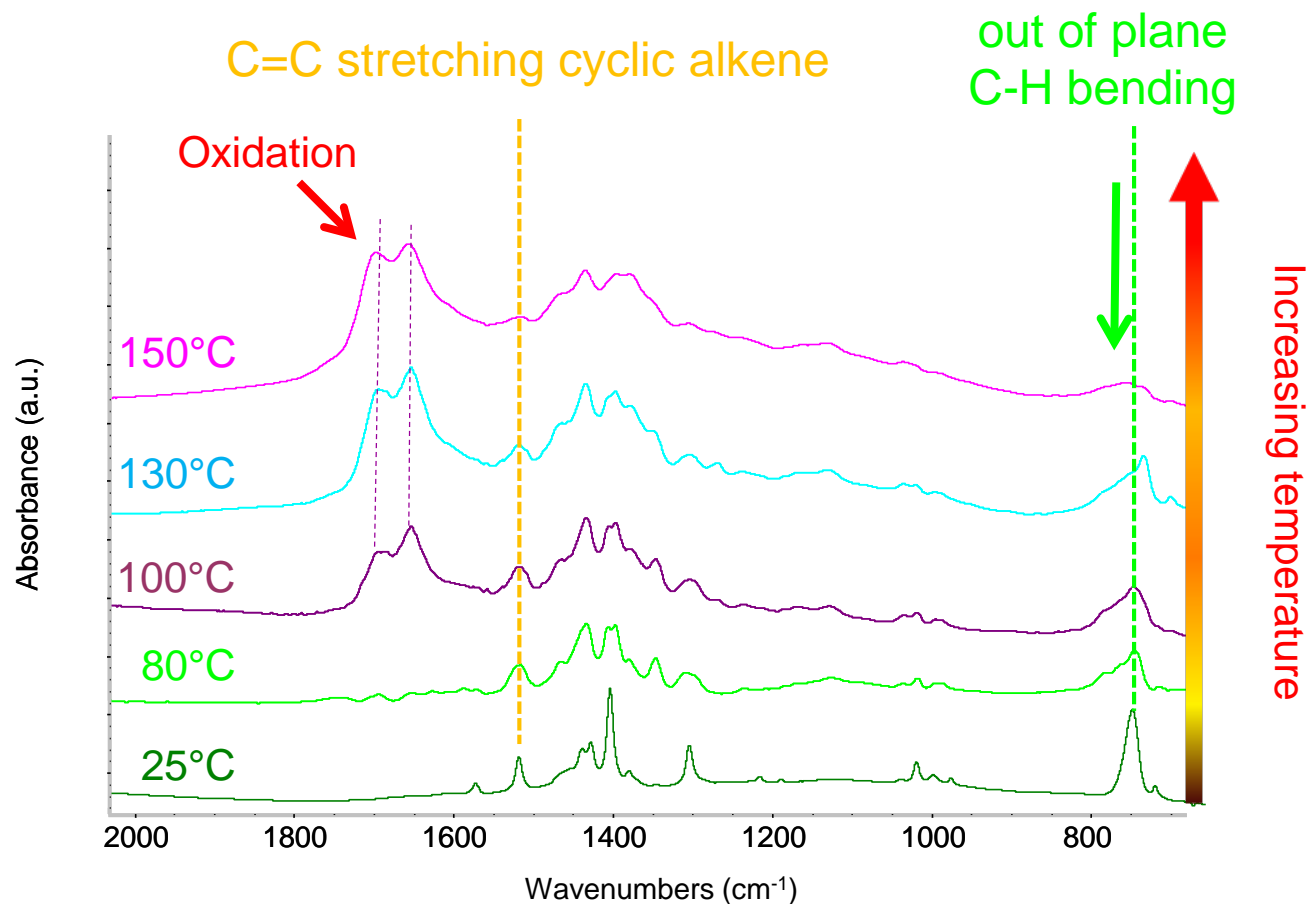
TMP + Air - From 25°C to 150°C



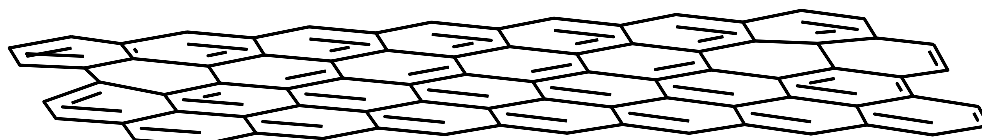
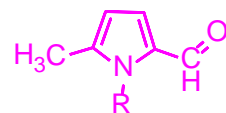
TMP + HSAG - from 100°C to 150°C



Oxidation products

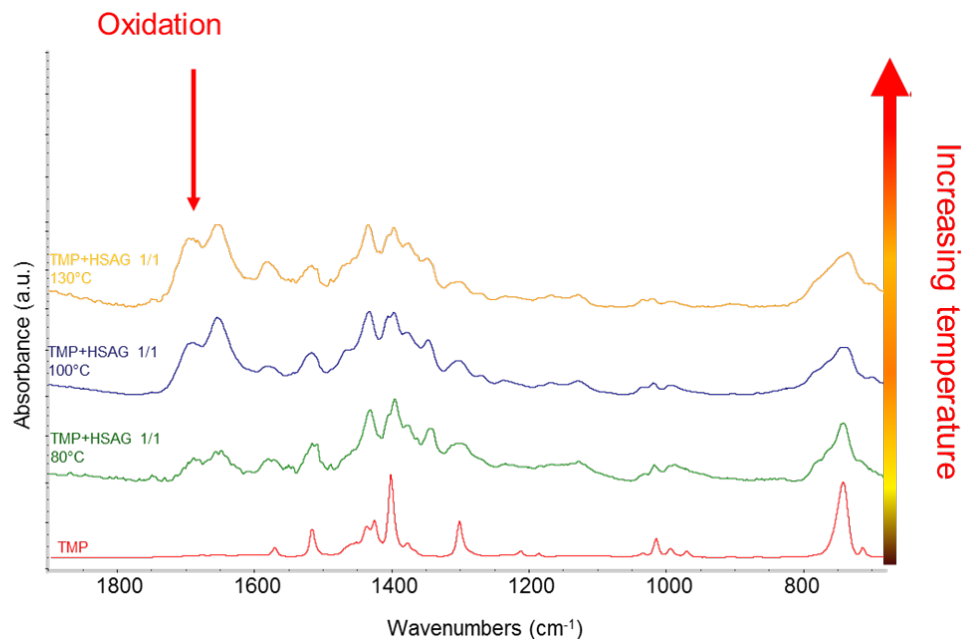


TMP oxidation product



1,5-dimethyl-1*H*-pyrrole-2-carbaldehyde

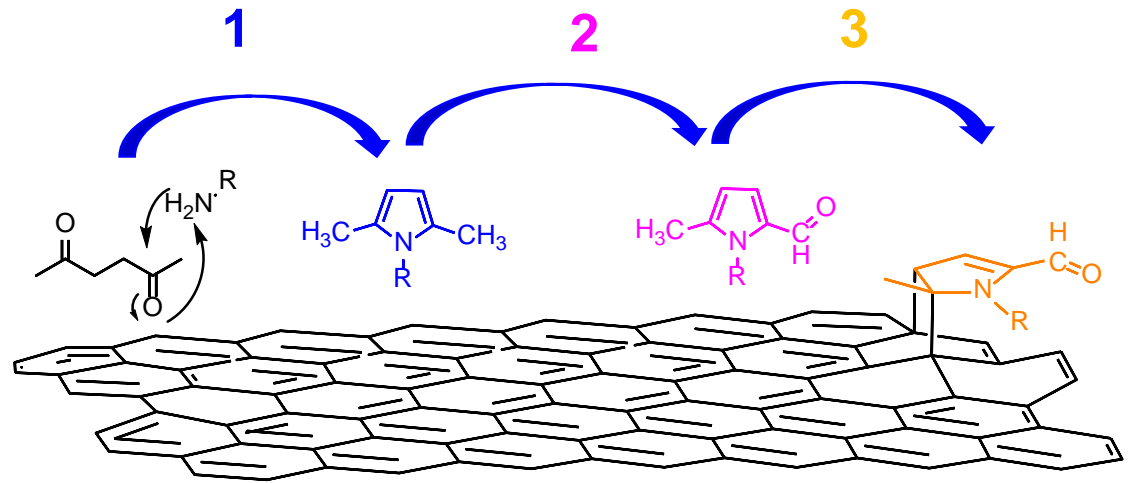
* Structure confirmed by means of NMR spectroscopy



FT-IR and ¹H-NMR spectroscopies; FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling

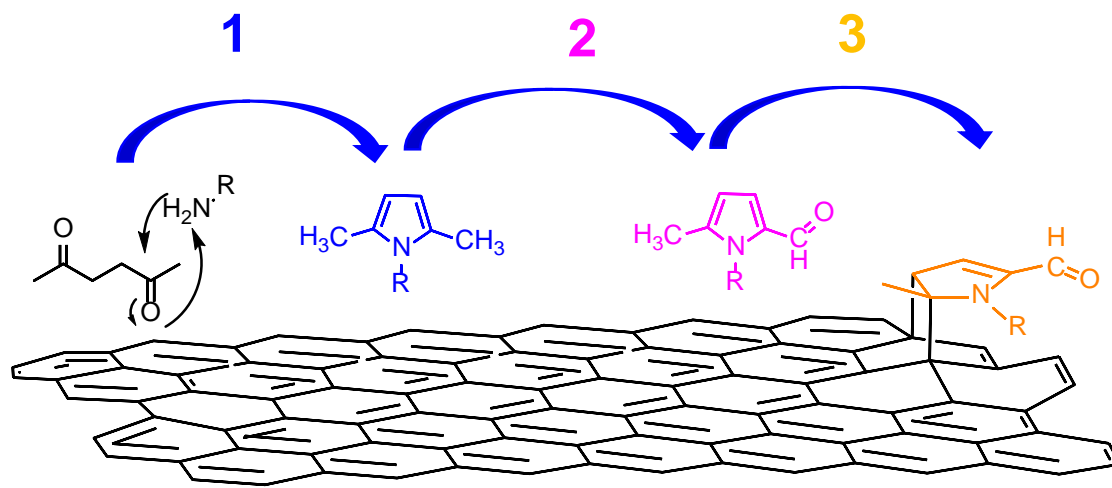
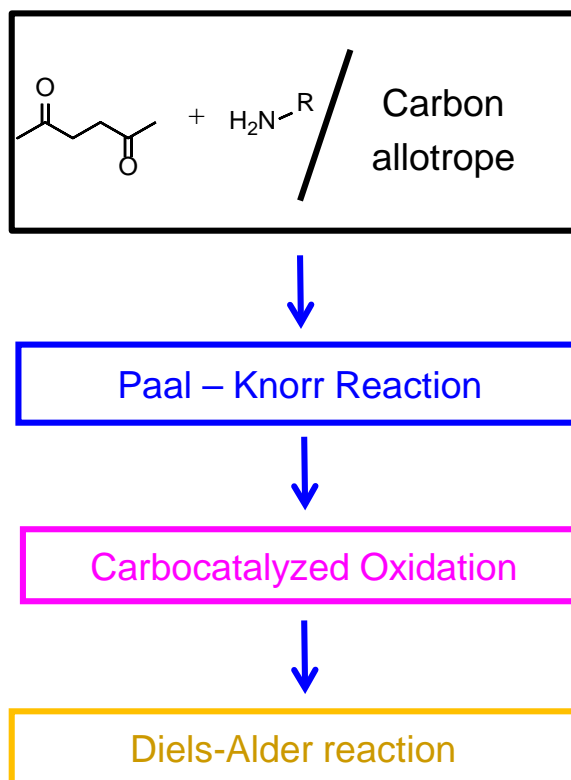
V. Barbera, L. Brambilla, M. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, and M. Galimberti, 2019. *Nanomaterials*, 9(1), p.44.

Hypothesis for the mechanism



Facile functionalization of carbon materials

Hypothesis for the mechanism

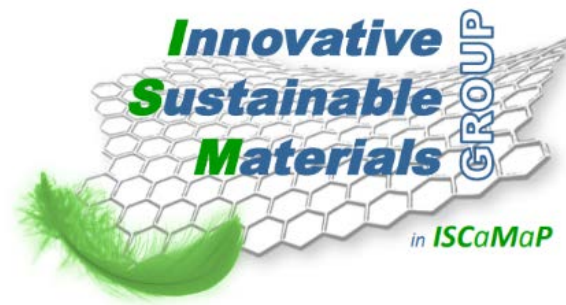


FT-IR and ¹H-NMR spectroscopies; FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling

V. Barbera, L. Brambilla, M. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, and M. Galimberti, 2019. *Nanomaterials*, 9(1), p.44.

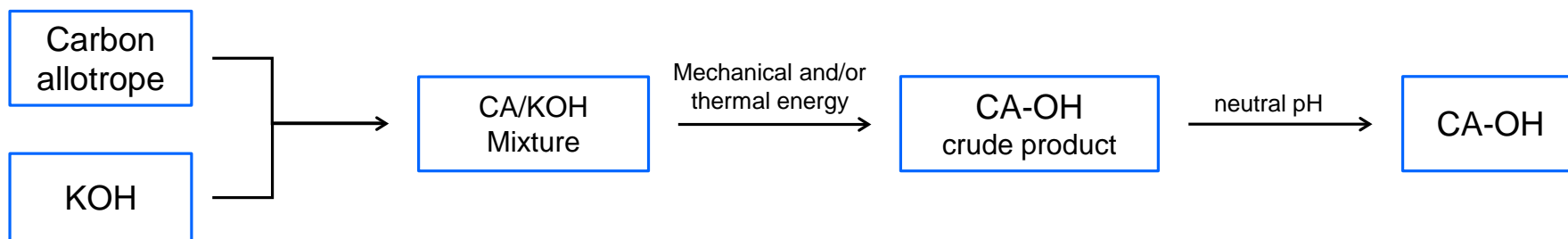
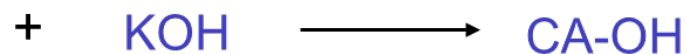
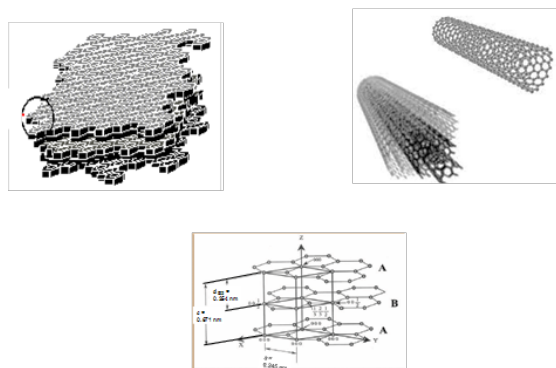
Functionalizing agents for sp^2 carbon allotropes from a large scale industrial product

KOH



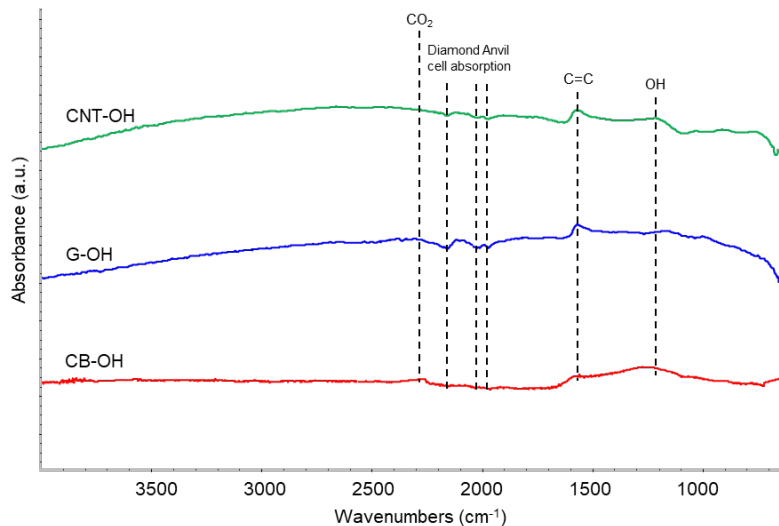
Synthesis of CA-OH

sp² carbon allotropes
(CA)

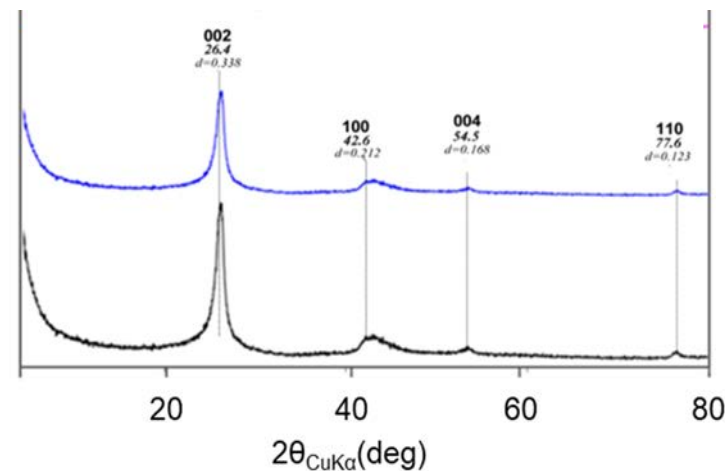


Synthesis of CA-OH

FT-IR



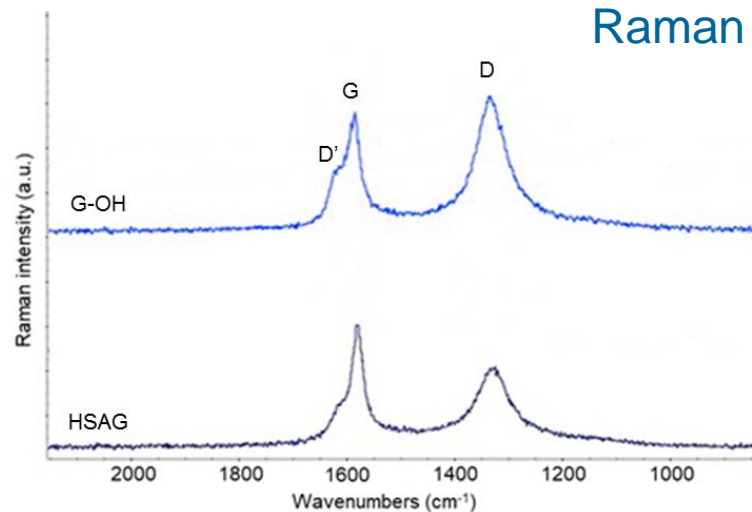
WAXD



Boehm titration

	CB	HSAG	CNT
Functional groups [mmol/g]	4.2	6.8	5.0

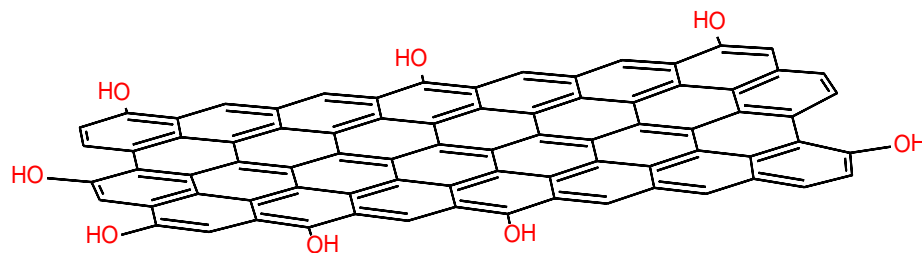
Raman



V. Barbera, A. Porta, L. Brambilla, S. Guerra, A. Serafini, A. M. Valerio, A. Vitale, M. Galimberti, [RSC Adv., 2016, 6, 87767-87777](#)

V. Barbera, A. Bernardi, G. Torrisi, A. Porta, M. Galimberti, [Elastomery, 2017, 21\(4\), 235-251](#)

Oxidation of HSAG with KOH



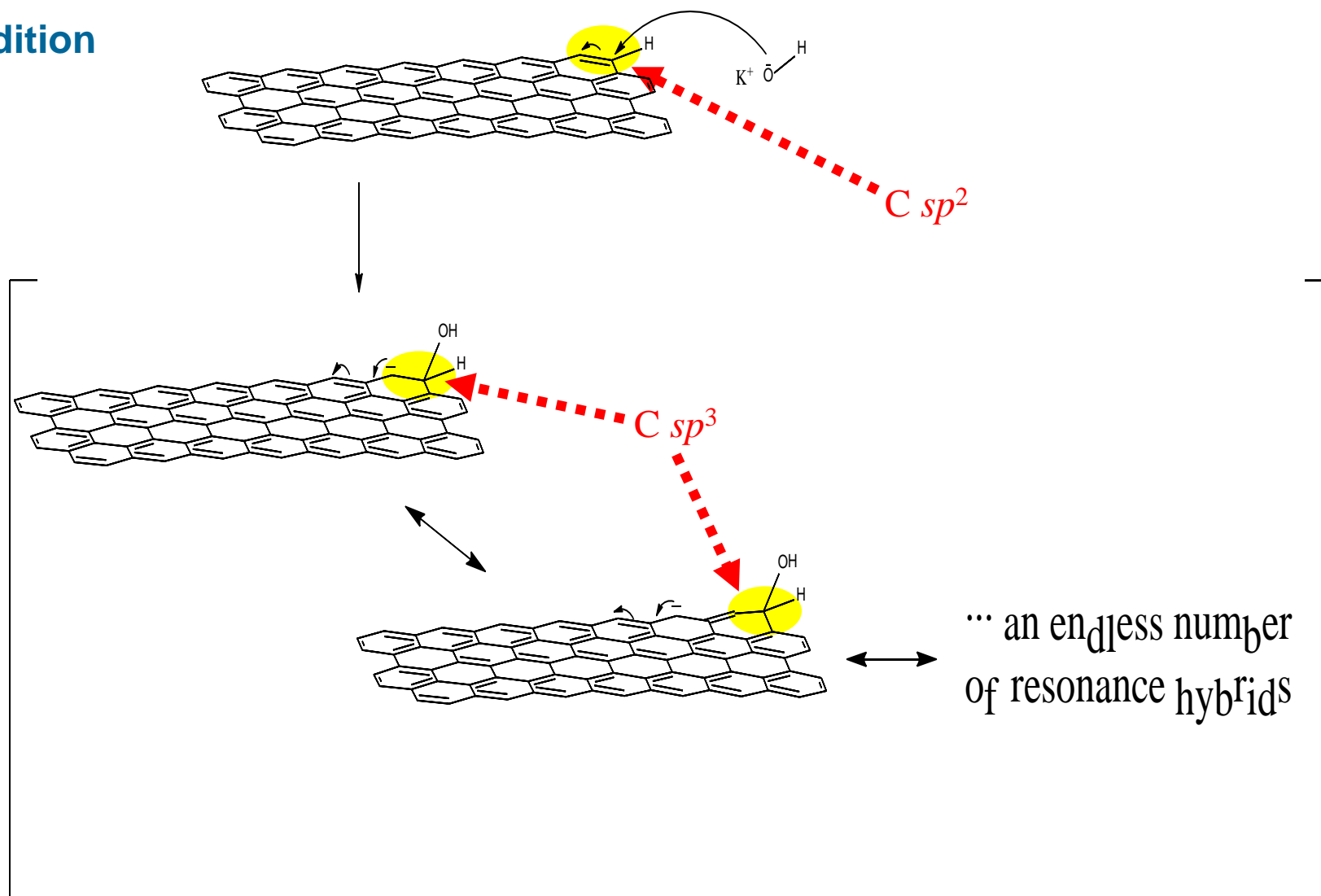
Polyhydroxylated
few layers graphene

- 👉 Selective introduction of OH groups up to 15 mass%
- 👉 In plane order substantially unaltered
- 👉 No expansion of interlayer distance

Preserved sp^2 hybridization

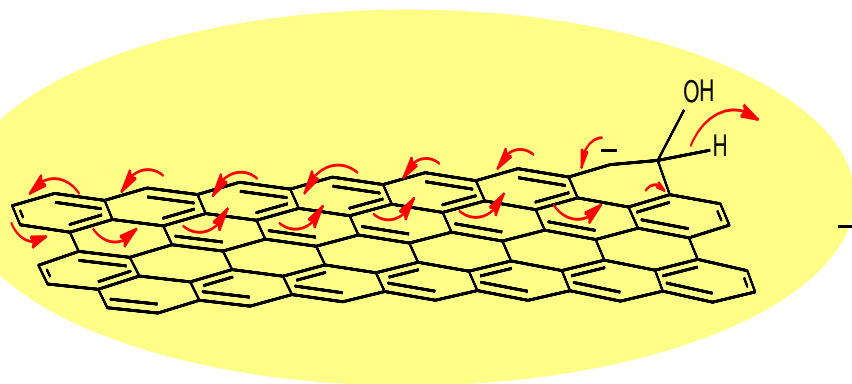
Oxidation with KOH – Proposed mechanism

Addition



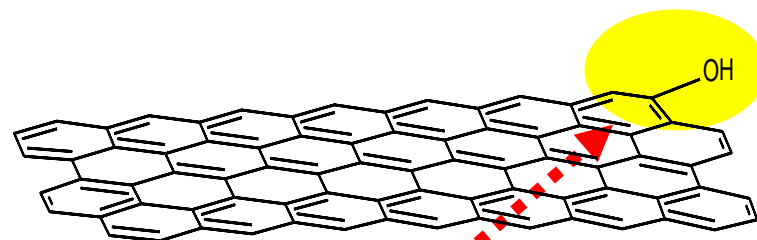
Oxidation with KOH – Proposed mechanism

Elimination



delocalization on the entire structure

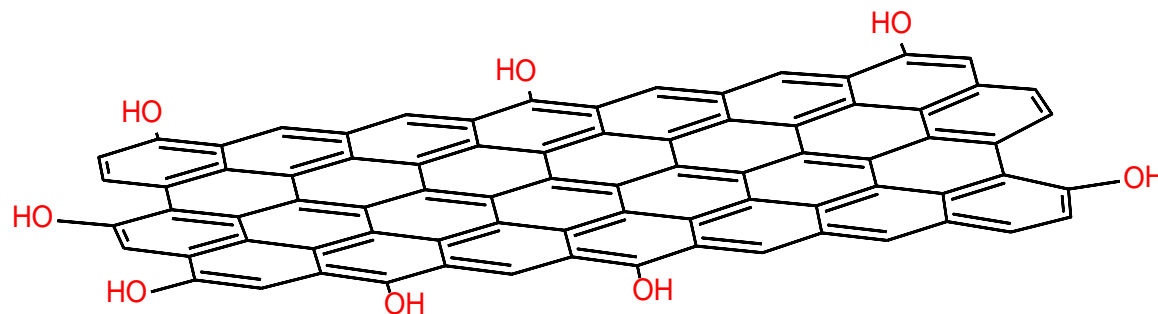
“wave effect”



$C\ sp^2$

More electronrich structure,
the oxygen lone pairs delocalized
on the polyconjugated system

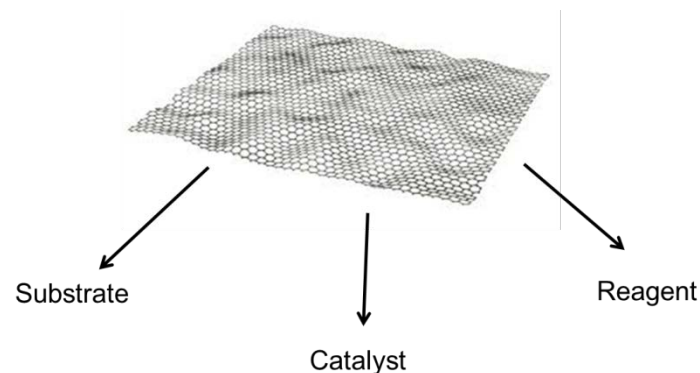
Synthetic strategy



Hydroxyl
few layer graphene



Polyphenolic few layer graphene
Platform chemical?

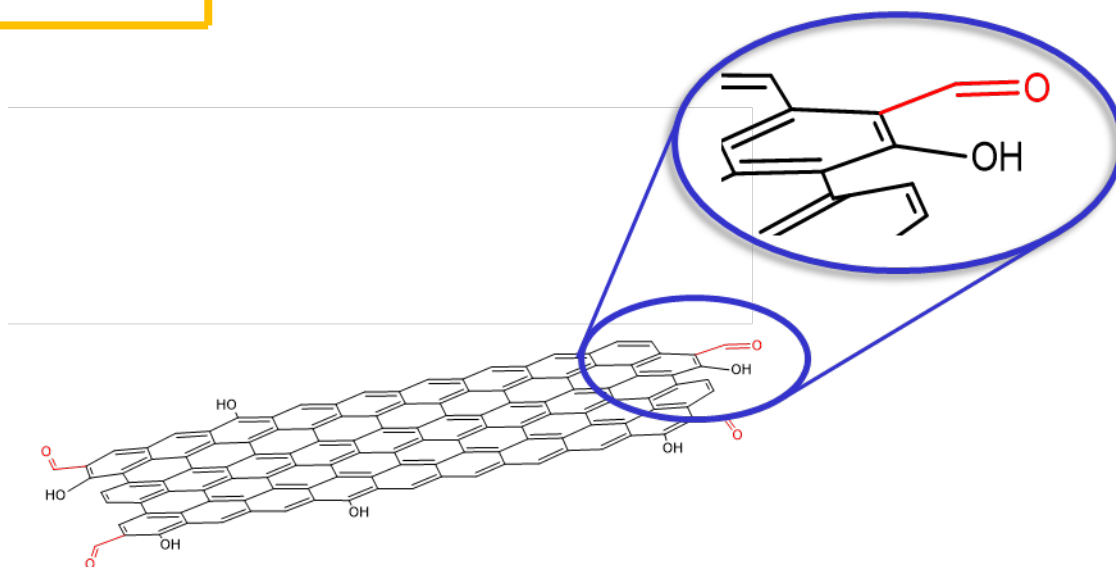


Selective introduction of oxygenated functional groups
by means of typical reactions performed on phenol ring

Selective introduction of aldehydic functional groups

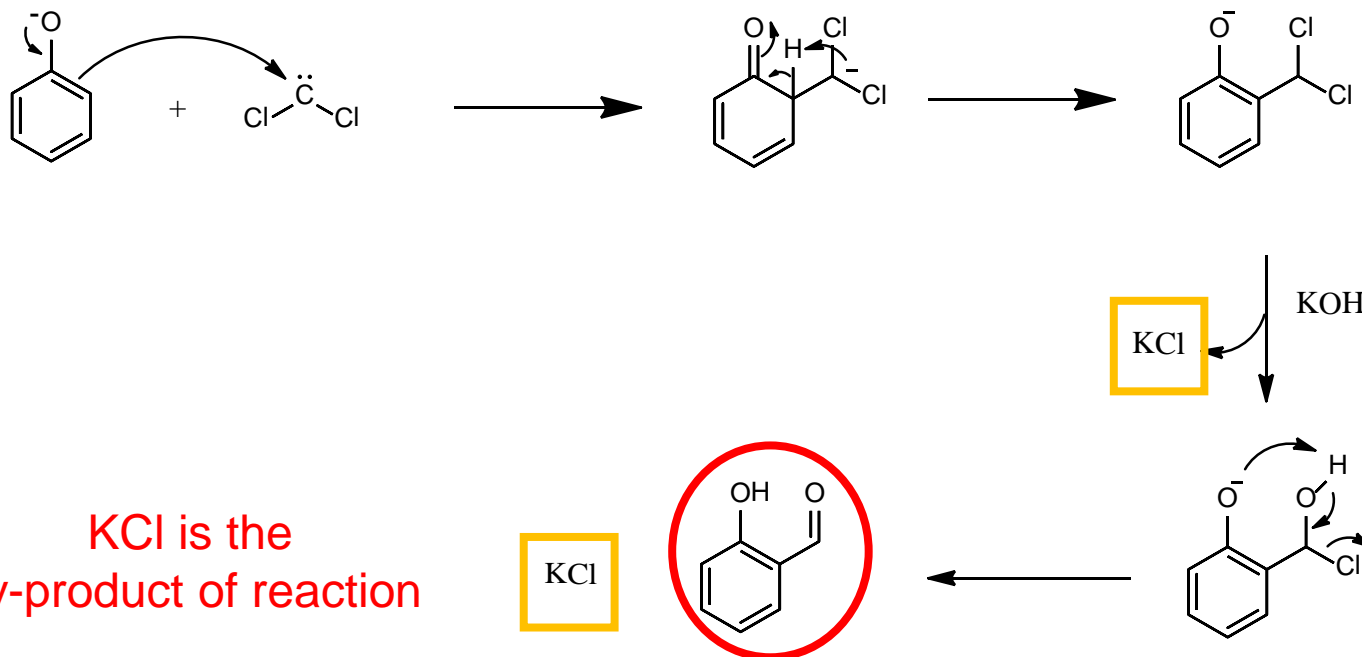


Selective ortho aldehyde



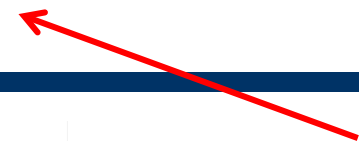
Reimer-Tiemann
reaction

Mechanistic pathway: the Reimer-Tiemann reaction



1 Aldehyde : 3 KCl \longrightarrow Detected in XRD patterns
molar ratio

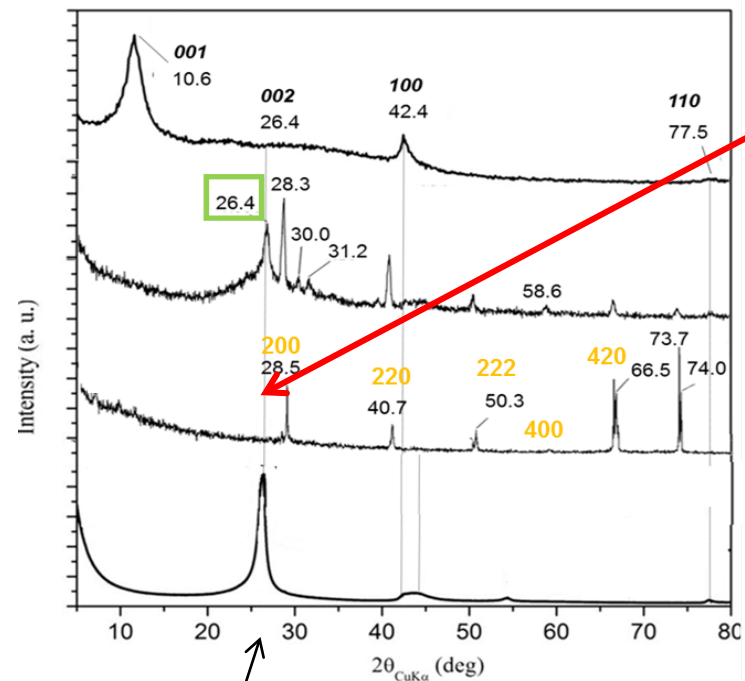
Exfoliation of nanographite



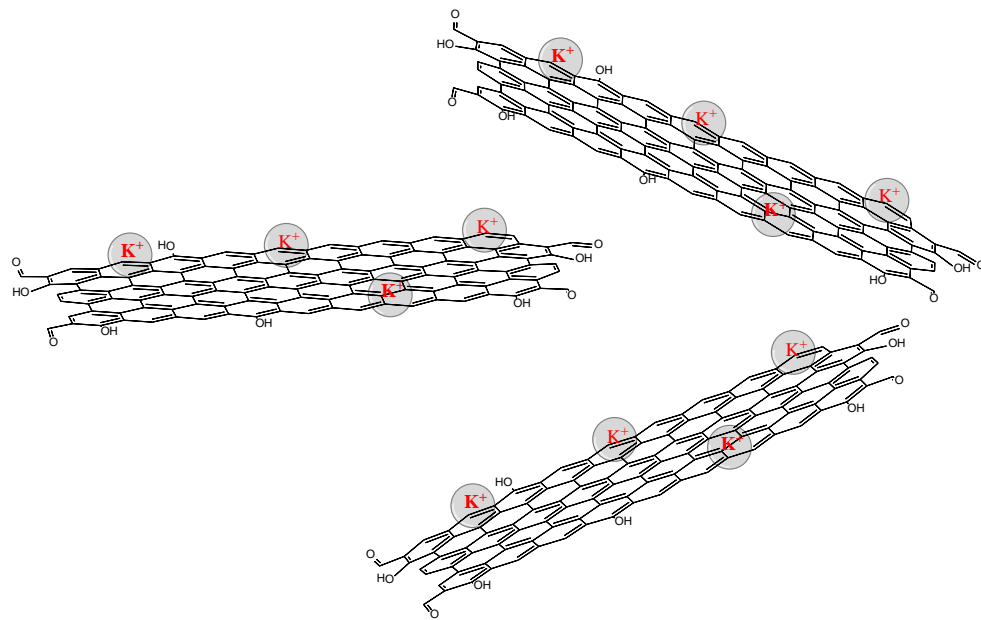
Absence of (002) reflection

G-CHO after KCl removal

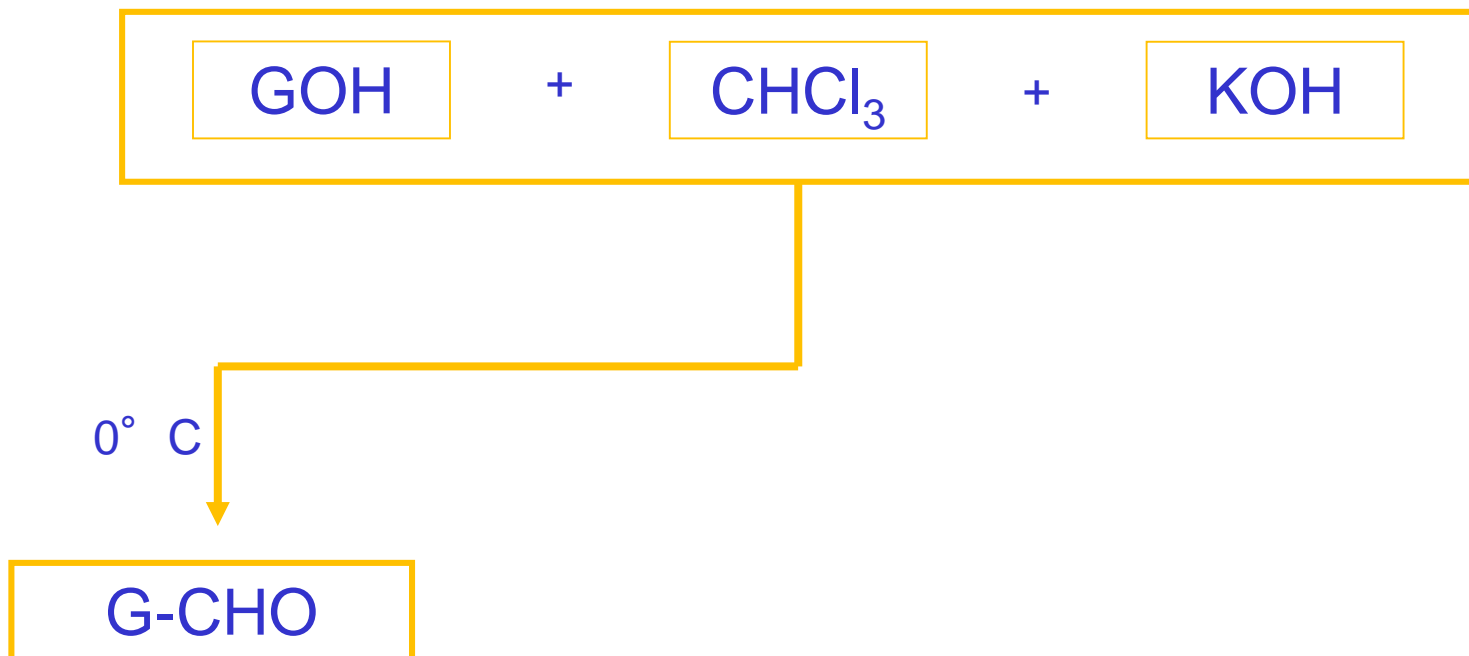
G-CHO in the presence of KCl



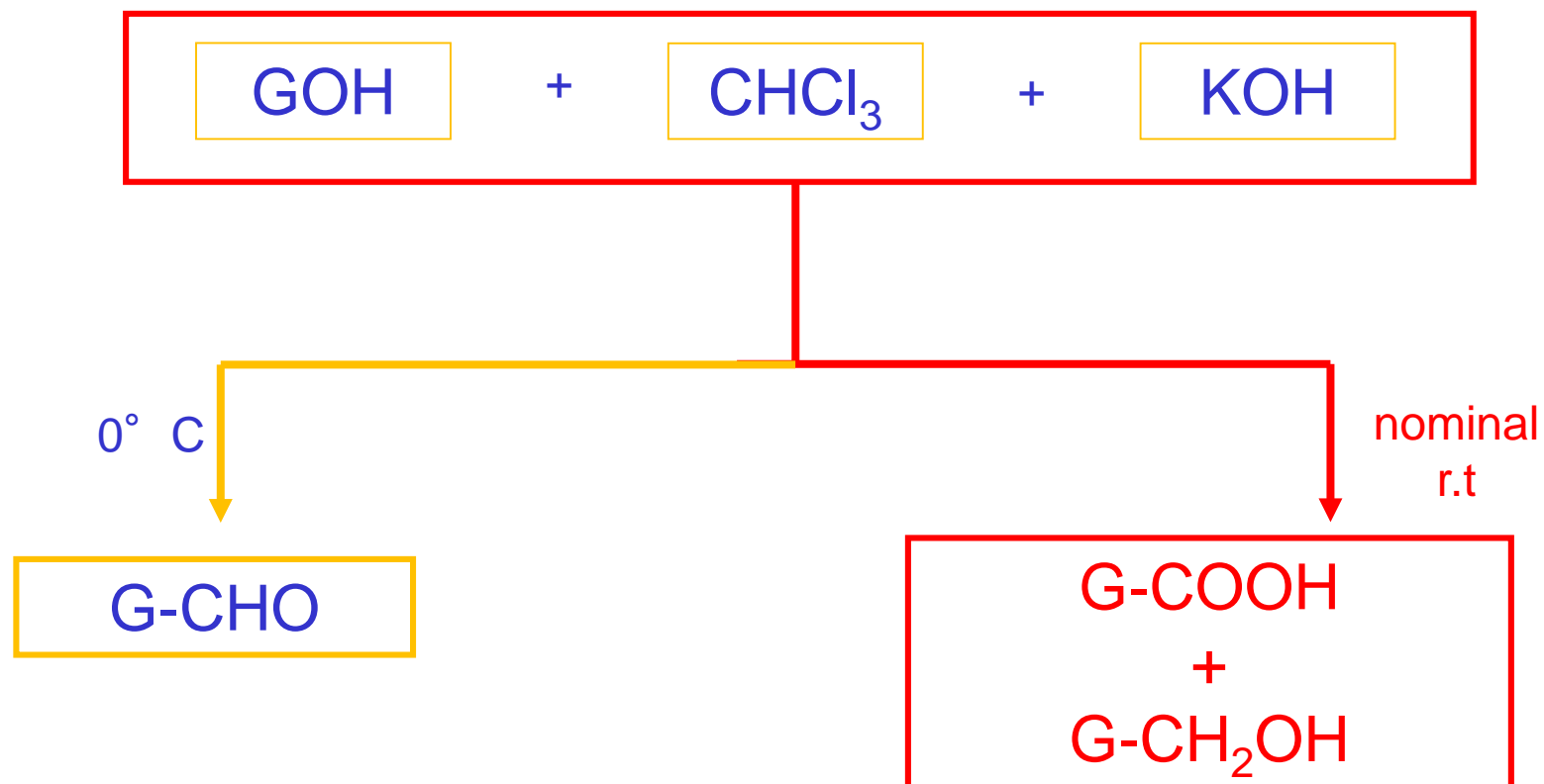
(002) reflection of graphite



GOH – Polyphenolic Graphite



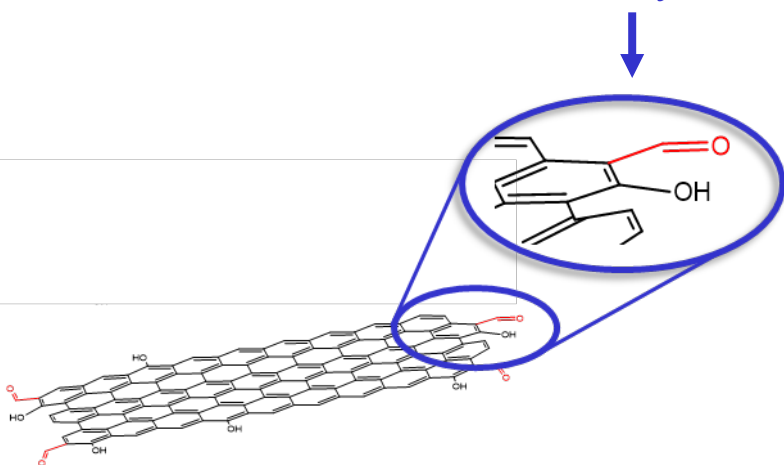
GOH – Polyphenolic Graphite



FT-IR, XPS analysis

GOH – Polyphenolic Graphite derivatives

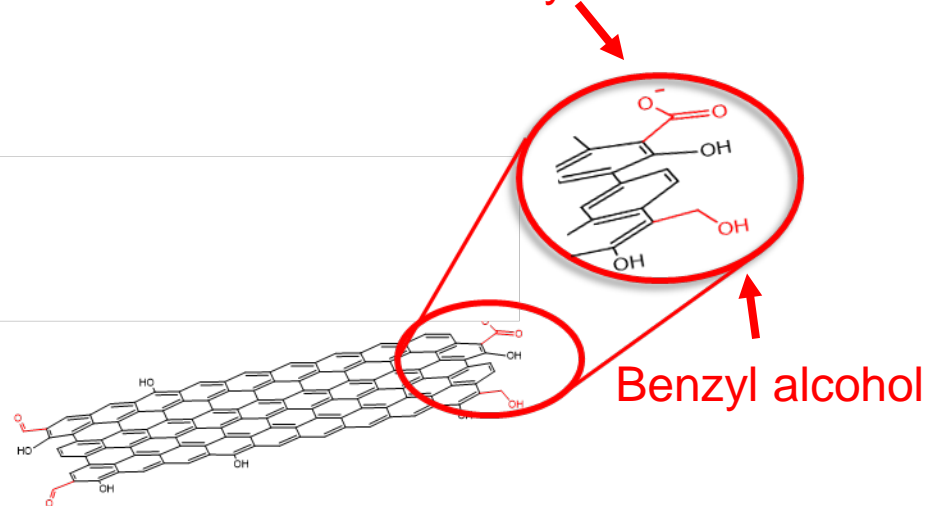
Aldehyde



G-CHO

Reimer -Tiemann

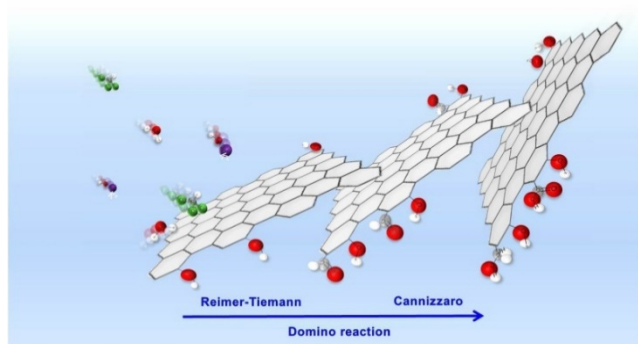
Carboxylate



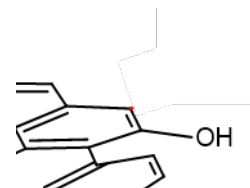
G-COOH
+
G-CH₂OH

Cannizzaro

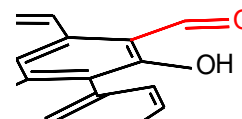
Reimer-Tiemann - Cannizzaro Domino reaction



G-OH

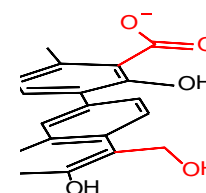


G-CHO



Reimer-Tiemann

G-COOH

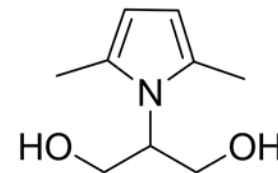


Domino Reimer-Tiemann/Cannizzaro



Functionalized sp^2 carbon allotropes in rubber compounds

- ➡ Better interaction/reaction
- ➡ Better dispersion
in the rubber matrix

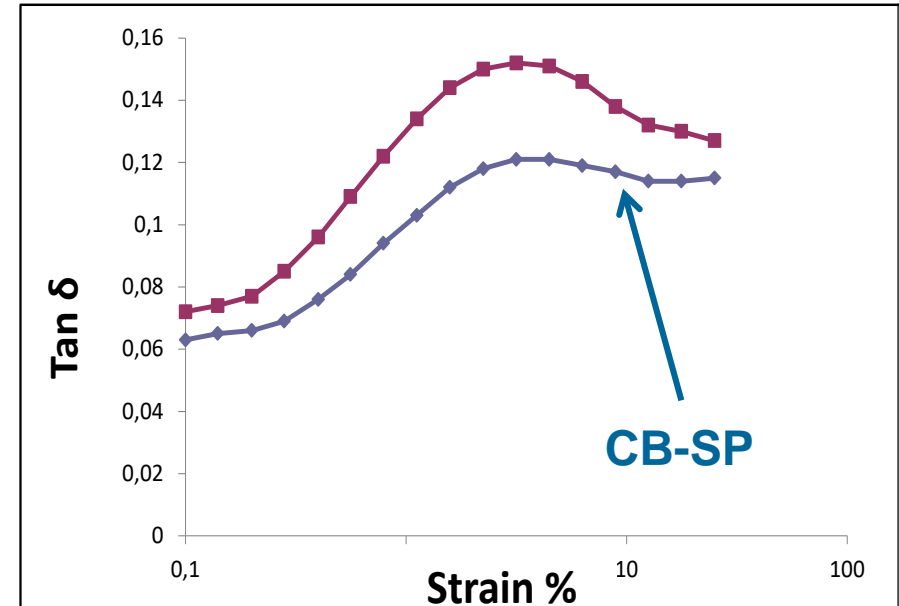
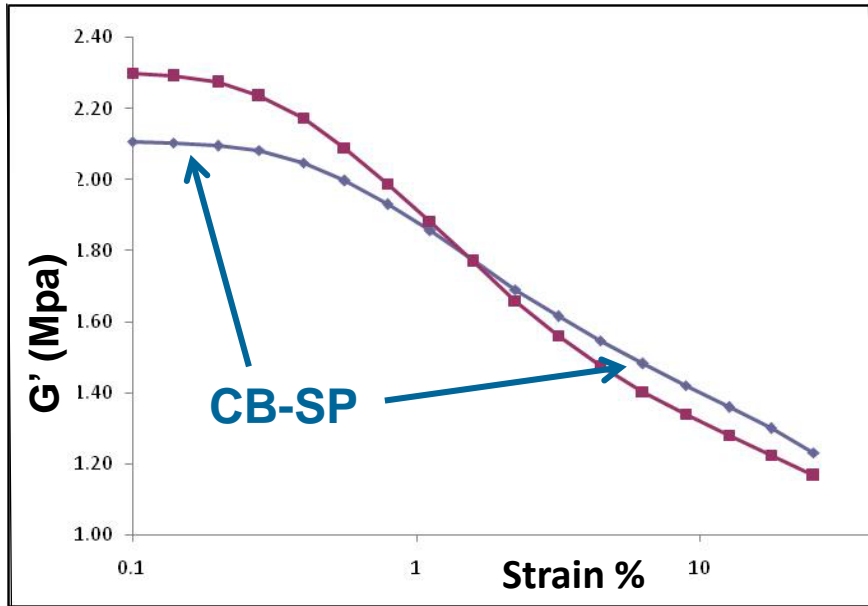


Recipes

Ingredient	Compound with CB	Compound with CB-SP
IR	50	50
BR	50	50
Silica	25	25
CB N326	25	0
CB N326-SP	0	27
CB N326	0	25
SP	0	2

Silane TESPT 2, Stearic acid 2, ZnO 4, 6PPD 2,
Sulphur 1.5, TBBS 1.8

Dynamic-mechanical properties



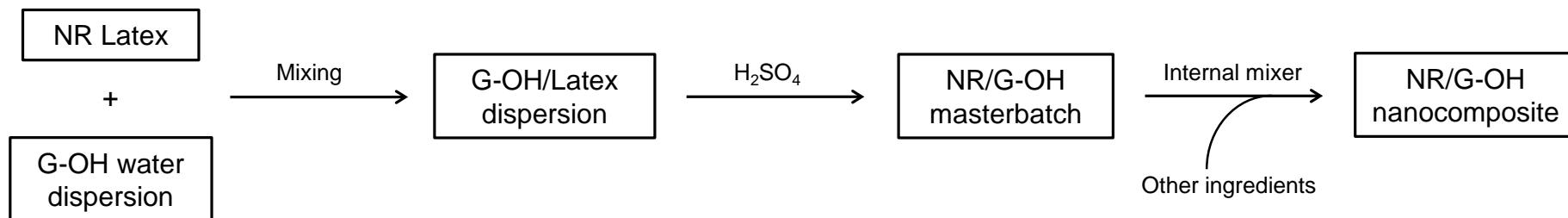
With CB-SP

- ☞ Lower Payne Effect and crossover of the curves
- ☞ Lower Tan delta

G-OH from HSAG+KOH in composites based on NR

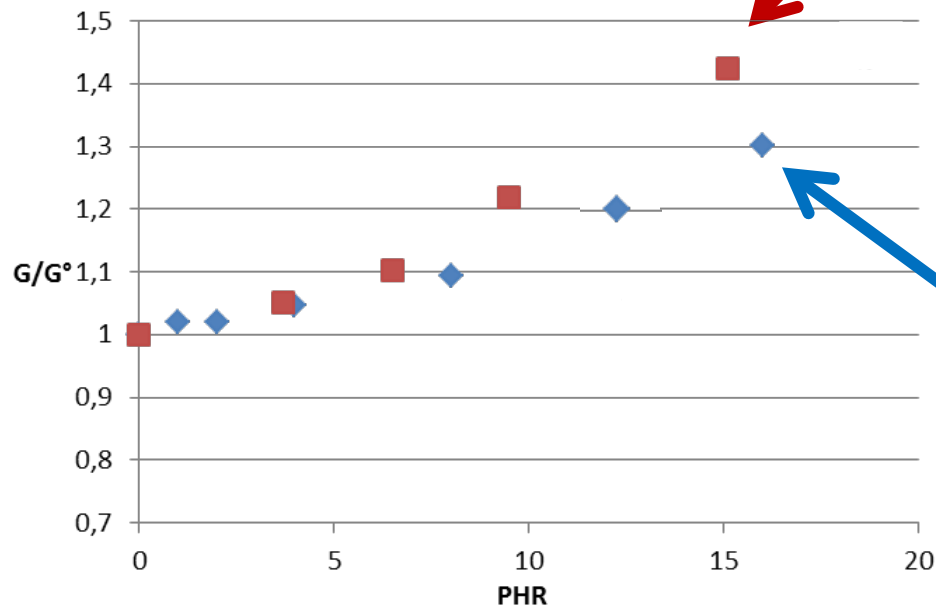
Ingredient	G-OH_0	G-OH_4	G-OH_7	G-OH_10	G-OH_12	G-OH_15	G-OH_25
NR	100	100	100	100	100	100	100
G-OH	0	3.7	6.5	9.5	12.3	15.1	25

Silane TESPT 2, Stearic acid 2, ZnO 4, 6PPD 2,
Sulphur 3, TBBS 1.8



G-OH from HSAG+KOH in composites based on NR

G/G⁰ ratios vs G-OH content

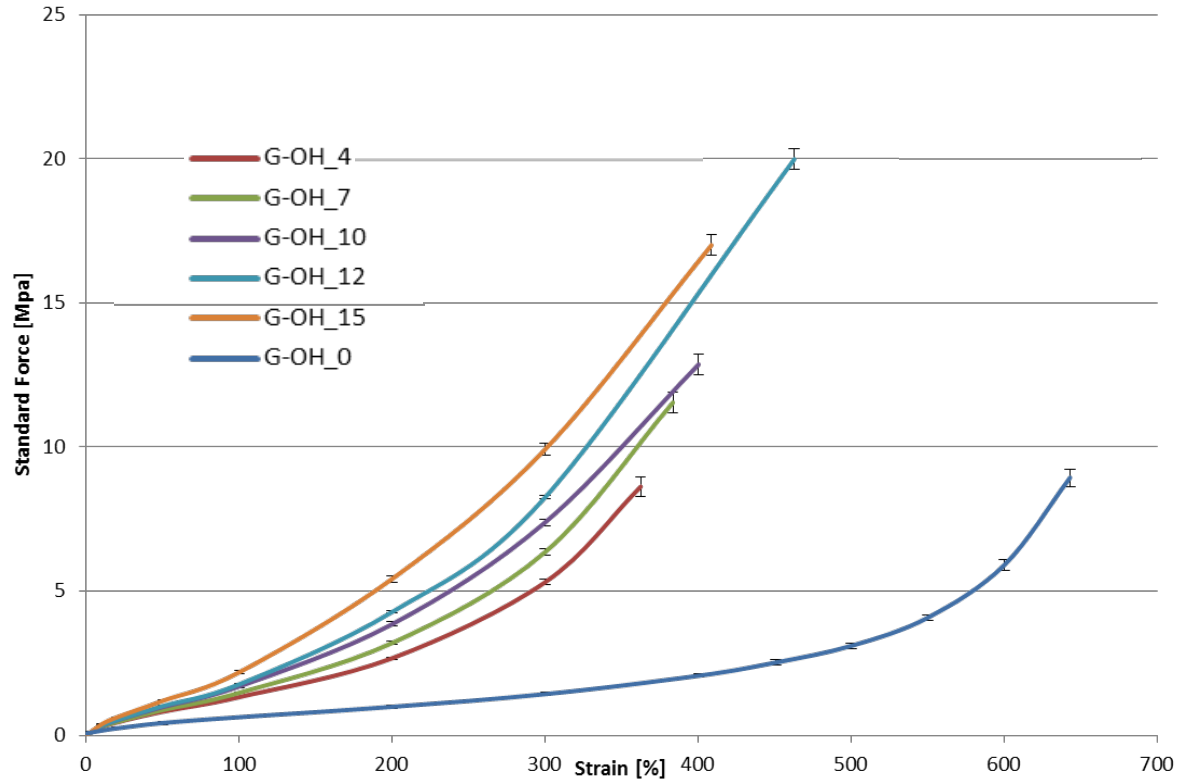


G-OH latex blending

HSAG melt blending

👉 Higher G' moduli with G-OH: better dispersion

Tensile properties

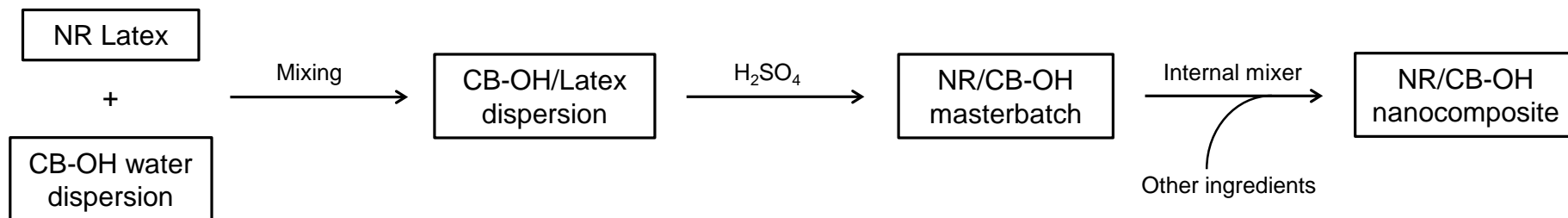


☞ Stresses at all elongations increase with G-OH content

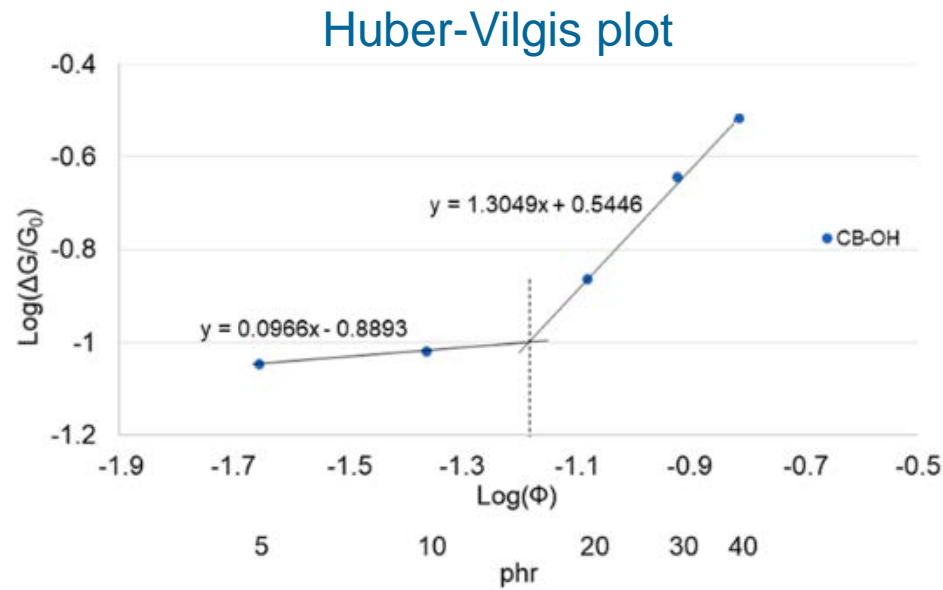
G-OH from HSAG+KOH in composites based on NR

Ingredient	G-OH_0	G-OH_4	G-OH_7	G-OH_10	G-OH_12	G-OH_15	G-OH_25
NR	100	100	100	100	100	100	100
CB-OH	0	3.7	6.5	9.5	12.3	15.1	25

Silane TESPT 2, Stearic acid 2, ZnO 4, 6PPD 2,
Sulphur 3, TBBS 1.8

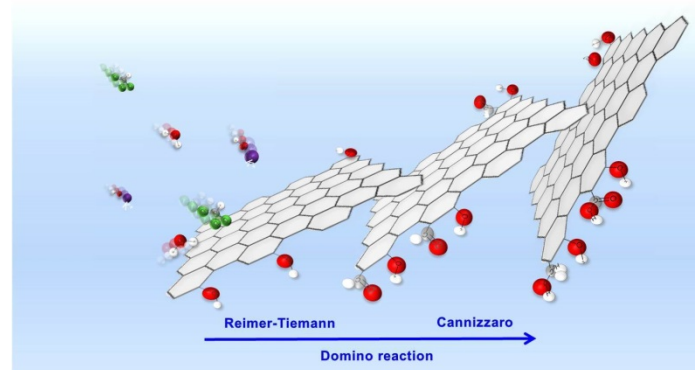
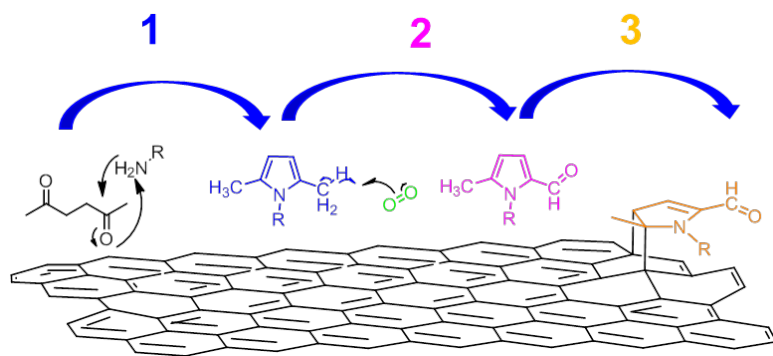
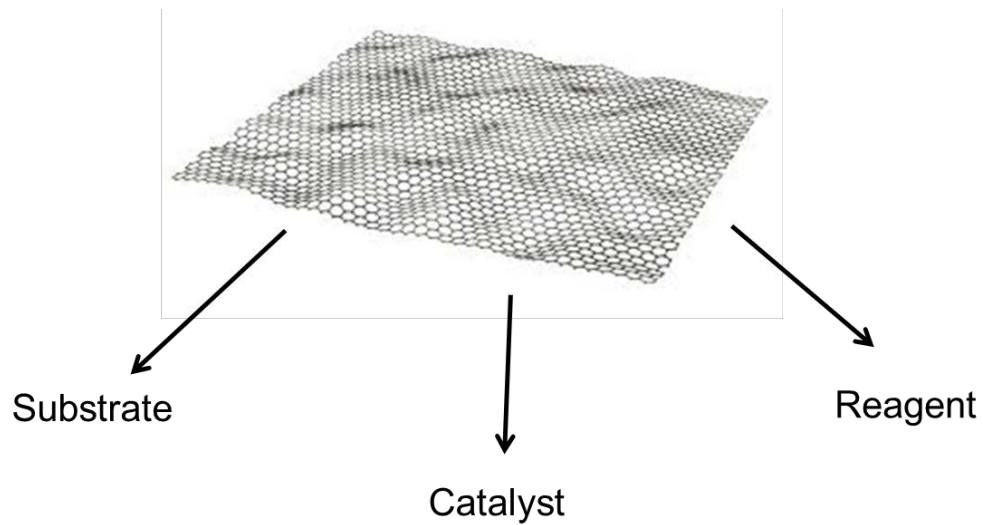


Natural rubber based nanocomposites

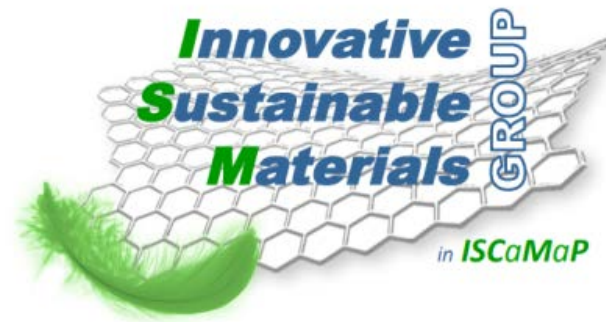


Percolation threshold (phr)	
CB	CB-OH
30 to 35	15

Conclusions



Thanks
for your attention!!



instagram: @ismaterials.polimi